The Second Annual

Undergraduate Research Symposium

Sponsored by the Western New York Section
of the American Chemical Society

and by

the Student Affiliates of the ACS, Canisius College Chapter

Saturday April 4, 2009

Canisius College, Buffalo, NY
Welcome to the Undergraduate Research Symposium!

The organizers and sponsors of this symposium are thrilled to convene this informal gathering, which, nonetheless, is a great opportunity to get a taste of the research efforts going on in Chemistry fields in our area. For students, this is a chance to show off your efforts and see a little bit of how scientists traditionally interact. For faculty members, it's good to be able to shake off some of the moss and ivy and get to know colleagues from other area programs. We welcome participants this year from five New York institutions and two from Ontario, Canada, and are pleased to have Dr. Nicola Brasch from the Department of Chemistry at Kent State University to give the keynote address.

Sincerely,

Timothy M. Gregg
Chair, 2009 Symposium Committee

2009 Symposium Organizing Committee

Chair: Dr. Timothy M. Gregg
Department of Chemistry and Biochemistry, Canisius College

Dr. Valerie A. Frerichs
Department of Chemistry, University at Buffalo, SUNY

Dr. Ronny Priefer
Department of Biochemistry, Chemistry and Physics, Niagara University

Dr. Bernard Pointner
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John R. Frost
Department of Chemistry and Biochemistry, Canisius College
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Schedule of Events

8:30-9:45 am  Registration / Poster setup / Coffee

9:45-11:00 am  Student Oral Presentations

11:00-12:00 pm  Keynote Presentation by Dr. Nicola Brasch,
Department of Chemistry, Kent State University
"Serendipity in Science: Knowing When You're On To a Good Thing"

12:00-1:00 pm  Lunch

1:00-2:00 pm  Student Poster Session I

2:00-3:00 pm  Student Poster Session II

3:30 pm  Symposium Awards and Closing Remarks
Our Keynote Speaker

Dr. Nicola E. Brasch received a bachelor's degree from the University of Otago in New Zealand in 1989, and her Ph.D. from the same institution three years later. She worked in Germany as a postdoctoral researcher at Phillips University in Marburg and at the University of Erlangen-Nuremberg, studying vitamin B$_{12}$ conjugates. She conducted research as a postdoctoral fellow at Colorado State University, working with Professor Richard Finke on some of the first isolable cobalt-thiolate coordination compounds as models of enzyme-B$_{12}$ complexes. In 1998 Dr. Brasch was named the first Rita Cornforth Research Fellow in the Department of Chemistry at The Australian National University. Dr. Brasch moved to Kent State University in 2003, and was promoted to Associate Professor in 2008.

Her work at Kent State has pursued more complex cobalamine enzyme-B$_{12}$ model complexes, including their potential use in vanadium-containing therapeutics for the treatment of diabetes. Interest in vanadium chemistry has also led her to the study of complexes of this metal in the unstable V(III) oxidation state. Her work has resulted in numerous publications, two patents for preparing and using B$_{12}$ derivatives as potential pharmaceuticals, an American Chemical Society PROGRESS/Dreyfus Lectureship, and a Mentorship Excellence Award from the Graduate Student Senate at Kent State University.
Oral Presentation Session
Room: Horan-O'Donnell Room 107
Moderator: Dr. Timothy M. Gregg
Canisius College

Abstract  Time  Speaker:
WNY01  9:45 am  **Thomas Fitzgibbons**, Jonathan Mann, Anthony Smith, Michael Detty, and David Watson
*University at Buffalo, SUNY*
"The optimization of light harvesting efficiency through the use of controlled aggregation and mixed monolayers of chalcogenoxanthylum dyes on titania for use in dye-sensitized solar cells"

WNY02  10:05 am  **Kin S. Yang**, Venkata Kandula and Donald C. Dittmer
*Syracuse University*
"Tellurium-triggered reactions with α-chloroacetyl derivatives of Evans’ chiral auxiliaries"

WNY03  10:25 am  **Danielle M. Raymond** and Ronny Priefer
*Niagara University*
"Multilayering of novel phenol-based polymers"

WNY04  10:45 am  **Tyler Bissett**, Jacqueline Gilmet, Hannes Leisch, David Ilceski and Tomas Hudlicky
*Brock University*
"Chemoenzymatic total synthesis of (-)-codeine and approaches to the synthesis of (+)-codeine"

Keynote Address  11:00 am  **Nicola E. Brasch**
*Kent State University*
"Serendipity in Science: Knowing When You're On To a Good Thing"
The optimization of light harvesting efficiency through the use of controlled aggregation and mixed monolayers of chalcogenoxanthylum dyes on titania for use in dye-sensitized solar cells.

Thomas Fitzgibbons, Jonathan Mann, Anthony Smith, Michael Detty, and David Watson

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY 14260-3000

ABSTRACT: This presentation will focus on excited-state electron injection from chalcogenoxanthylum dyes into nanocrystalline titanium dioxide electrodes. The dyes undergo controlled aggregation on TiO$_2$ surfaces. The nature and extent of aggregation, and therefore the optical properties of the dyes, are tunable by varying the structure of the dyes. Mixed monolayers of H-aggregating, J-aggregating, and non-aggregating dyes were used to broaden the absorbance spectra and enhance the light-harvesting efficiency of the dye-sensitized electrodes. The electron transfer process was characterized by photoelectrochemical techniques and fluorescence spectroscopy. Ground-state and excited-state potentials were measured to quantify the driving force for electron injection. Spectral broadening and electron injection from oxidized dye into the TiO$_2$ semiconductor was achieved by controlling the aggregation of chalcogenoxanthylum dyes on an anatase TiO$_2$ surface.
Tellurium-triggered reactions with $\alpha$-chloroacyl derivatives of Evans’ chiral auxiliaries

Kin S. Yang, Venkata S. Kandula and Donald C. Dittmer

Department of Chemistry, Syracuse University, Syracuse, NY 13244

ABSTRACT: Reactions of $\alpha$-chloroacyl derivatives of Evans' chiral oxazolidinone auxiliaries with telluride ion are currently being investigated as a method of forming enolates rapidly and quantitatively. $\alpha$-Chloropropionyl diastereomers are separable by chromatography and their individual reactivities are explored. The resulting enolates readily react with aldehydes in a stereoselective fashion to yield anti-aldol adducts in moderate yields (60-65%), and good diastereoselectivity (~7:1). Advantages of our telluride methodology include fast reaction times (< 1 h), and generation of an enolate without the use of a strong base. X-ray analysis of one of the chloropropionyl diastereoisomers and of the 4-nitrobenzoate ester of the aldol product derived from it reveals the stereochemistry of the reaction sequence.
Multilayering of novel phenol-based polymers

Danielle M. Raymond and Ronny Priefer

Department of Biochemistry, Chemistry, and Physics, Niagara University,
Niagara University, NY 14109

ABSTRACT: Phenol based polymers have shown promising results as anti-microbial agents through an analysis of multi-layered quartz slides. A novel four step synthesis has been implicated to create unique phenol based polymers using free radical polymerization. The polymers are distinctive due to a number of different electron withdrawing substituents placed on the third position of the phenyl ring. The polymers have been successfully layered onto quartz slides with specific binding affinities based on these substituents.
Chemoenzymatic total synthesis of (-)-codeine and approaches to the synthesis of (+)-codeine

Tyler Bissett, Jacqueline Gilmet, Hannes Leisch, David Ilceski and Tomas Hudlicky

Department of Chemistry and Centre for Biotechnology, Brock University, St. Catharines, Ontario L2S 3A1

ABSTRACT: The application of biocatalytic methods to target-oriented synthesis has resulted in short, enantioselective syntheses of a number of natural products such as pancratistatin, carbohydrates and morphine alkaloids as well as unnatural analogues of these biologically active compounds. A chiral dihydroxylation of β-bromoethylbenzene generates a syn-diene diol, which is utilized as starting material in the total synthesis of (-)-codeine. This synthesis features two intramolecular Heck cyclizations and an oxymercuration as key steps. An approach towards the synthesis of (+)-codeine is also presented, with key steps including a Mitsunobu inversion and intramolecular Heck reaction.
Student Poster Session I
Room: Horan-O'Donnell 1st Floor
Time: 1:00-2:00 PM

Abstracts
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Student Poster Session II
Room: Horan-O'Donnell 1st Floor
Time: 2:00-3:00 PM

Abstracts
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Synthesis of spermidine and spermine derivatives as potential inhibitors of *Trypanosoma cruzi* trypanothione reductase

*Mark Saric, Thomas Edd, Michael St.Phillips, Nicholas Karney and Mary O’Sullivan*

ABSTRACT: Trypanothione reductase (TR) is an enzyme found only in members of the Trypanosomatidae family. Several organisms belonging to this family are parasitic protozoa responsible for severe diseases including African trypanosomiasis (*Trypanosoma brucei rhodesiense* and *T. b. gambiense*), Chagas disease (*T. cruzi*) and leishmaniasis (*Leishmania major*, *L. tropica* and other species). Trypanothione reductase catalyzes the reduction of trypanothione (a glutathione-spermidine conjugate) by NADPH. Dihydrotrypanothione plays a vital role as a reducing agent in several metabolic processes in trypanosomatids. Several previous reports have shown that certain polyamine derivatives are inhibitors of TR, including spermine and spermidine derivatives with naphthylmethyl and 3-phenylpropyl substituents. We report the syntheses of several novel analogs of these compounds that contain *N*-melamine or *N*-carboxamidino substituents. These new compounds were designed as potential inhibitors of TR and trypanocidal agents.
Synthesis of lactone analogs of pramanicin for bioactivity analysis

Syed A. Hasan and Paul Harrison

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ABSTRACT: Pramanicin (1) is a natural product isolated in 1994 as an anti-fungal agent from the bioassay-directed fractionation of a Stagonospora fungus at Merck labs. It has been found that 1 possesses biological activity in nanomolar concentrations.

Structure of pramanicin (1) and its analogs 2, 3 and 4

In light of previous work with pramanicin analogs in the Harrison group, it is proposed that the minimal pharmacophore of 1 comprises one of: a) the N-H bond in the lactam, b) the primary alcohol on the head group, or c) the length of the alkyl side chain.

To probe these possibilities, three analogs of pramanicin (2, 3, and 4) were synthesized using a strategy of Claisen condensation and α-hydroxylation of the resulting β-ketoester. 3 and 4 have been synthesized in overall isolated yields of 25% and 19%, respectively. An intermediate en route to 2 has been synthesized in 16% overall isolated yield.

Steric and electronic effects of substituents on the rate of allene cyclopropanation

Mark K. Farrugia, John R. Frost and Timothy M. Gregg

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ABSTRACT: Enantioselective cyclopropanation of monosubstituted allenes can be an efficient process, giving good yields and providing alkylidene cyclopropanes in high enantiomeric excess. Adding a second substituent onto the allene has a detrimental effect on the yield of the reaction, probably because steric crowding during approach of the allene to the reactive carbenoid intermediate slows cyclopropanation to the point that competitive side-reactions dominate. It is likely that electronic effects of substitution onto phenyl allenes are small, since the cumulated diene geometry precludes direct resonance interactions with the developing cyclopropane ring. We present evidence that suggests the stabilizing effect of a silyl substituent, in contrast, can greatly accelerate the reaction, presumably through stabilization of cationic character in the transition state β- to the silicon atom. This report compares cyclopropanation rates using substrate competition, and shows that the rate enhancement effect of a silyl group can overcome the rate-retarding effects of steric crowding.
ABSTRACT: Reductive amination is a chemical reaction commonly used in the pharmaceutical industry. In this reaction, a carbonyl group is converted to an amine via an imine intermediate. The rate-determining step of this process is the formation of the imine. A major reagent necessary for the completion of the reaction is a hydride source, commonly sodium cyanoborohydride (NaCNBH₃). The objective of this research is to compare the efficacy of NaCNBH₃ with silica-bound cyanoborohydride (Si-CBH) as hydride sources in reductive amination.

For each comparison, one equivalent of a ketone or aldehyde was reacted with two equivalents of an amine for 24 hours in tetrahydrofuran (THF) and gas chromatograph (GC) was run to monitor the progression of the reaction. The results of the GC spectra were used to compare the conversion of reactants to product with the reactions using NaCNBH₃ and the reactions using Si-CBH.

Work thus far has revealed that reactions using Si-CBH as a hydride source showed significant improvement, averaging about 25%, over those using the NaCNBH₃. Future work entails expanding the library of completed reactions to further validate these findings.
BF$_2$ Chelated azadipyrromethene dye derivatives: synthesis and fluorescent activity on HeLa cells in culture

Justin R. Griffiths, Graham Skelhorne-Gross, Robert S. Greene and Ronny Priefer

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ABSTRACT: BF$_2$ chelated azadipyrromethene dyes fluoresce in the near infrared and have potential applications in photochemical therapy. When irradiated near 600 nm these aza-BODIPY dyes react with O$_2$ to form a reactive singlet oxygen species. A small library has been synthesized via a four-step process, with varying substituents on the aromatic ring of the starting benzaldehyde and acetophenone. An in vitro study has also been conducted to look at the level of cell death when irradiated with near infrared light to investigate their therapeutic effectiveness and practical applications. Apoptosis as well as necrosis has been observed for many of these potential chemotherapy agents.
Novel cubane-based chiral ligand: uses on cyclopropanation and Henry reactions.

Michelle L. Ingalsbe and Ronny Priefer

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ABSTRACT: A novel chiral cubane-based ligand was prepared in five steps using dimethyl-1,4-cubane carboxylate as its precursor. Its application in asymmetric copper(I)-catalyzed cyclopropanation of styrene with ethyl diazoacetate has been screened, as well as on the Henry reaction with nitrobenzaldehyde and nitromethane. The bulkiness of the ligand has proved to be essential in enantioselectivity, suggesting that interaction with the catalyst is difficult compared to a benzene-based ligand.
Using RNase H to improve RNA secondary structure prediction

Chantal B. Bartels, Andrew D. Kauffmann, Ryan J. Campagna, and Jessica L. Childs-Disney

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ABSTRACT: RNA has many essential cellular functions, including encoding for proteins, participating in the synthesis of proteins, and regulating gene expression. Like proteins, the function of an RNA is related to its structure. Thus, accurately predicting RNA structure is important. Computational methods are available to predict RNA secondary and tertiary structure. One program, RNAstructure, uses free energy minimization to predict secondary structure and predicts 73% of base pairs correctly in domains with fewer than 700 nucleotides. Improvements can be made if experimental constraints from enzymatic mapping or chemical modification are used. Herein, we present a simple method using RNase H and randomized DNA oligonucleotides that improves secondary structure prediction. This method should be applicable to any RNA.
Copper(II) catalyzed carboamination of alkenes; synthesis of benz[f]indoles

Weng Siong Tham, Imranul Haque, Maria M. Manzoni and Sherry R. Chemler

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ABSTRACT: Benz[f]indoles are a common motif in biologically active compounds. These biological compounds have been known to exhibit antitumor activity. We are able to use our copper(II) catalyzed carboamination reaction to synthesize these biologically active compounds. The substrate scope of this reaction has been extended to aliphatic sulfonamides that do not have an aromatic ring attached directly to the nitrogen. This method allows a quick and efficient access to the core of the benz[f]indoles.
Do point mutations evoke disperse entropic changes throughout a protein domain?


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ABSTRACT: The 56 amino acid B1 domain of Protein G from Streptococcus exhibits thermal stability over a broad range of temperatures. It is known experimentally that the thermal stability of the protein changes, sometimes dramatically, when amino acid substitutions are introduced at position 53. Experimental attempts to attribute this to locally-induced perturbations, such as steric effects and solvent interactions, have failed. To explore and quantify the remaining possibility, that point mutations have significant non-local effects on protein structure, we performed molecular dynamics (MD) simulations on the wild type B1 domain and several of its mutants. We then re-sampled, with replacement, the mutant trajectories one thousand times, each time subjecting the resulting conformations to principal component analysis of their inter-Cα distances, followed by Procrustes-rotation of the factors to best fit those of the wild type. Our results suggest that the thermal stability of the mutants decreases as the fit of their Procrustes-rotated factors to the wild type B1 domain deteriorates. We will discuss how figures such as that illustrated below demonstrate that extreme deviations of fit are attributable to amino acid residues within secondary structure elements far-removed from the site of mutation.

Deviations from the from the wild type resulting from mutation at position 53 in B1 domain of Protein G. Plotted is the Procrustean-rotated principal components of the mutants deviation from the wild-type principal components of 1000 trajectories. Top panel: T53P (T_m<10°C); Bottom panel: Thr (T_m=69°C).
WNY14

Direct NMR evidence for bromide ion coordination to transition metal substituted polyoxometalates in nonpolar solvents.

Mark Makar, Kyle Malstrom, Brian Tyler, Steven Szczepankiewicz and Mariusz Kozik

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ABSTRACT: Our work in the past demonstrated that structures of Transition Metal Substituted Heteropoly Tungstates, TMSHT, in nonpolar solvents are more complex than published in the literature. As the nonpolar solvent is dried, several new signals appear in the 31-P NMR spectrum. Our interpretation has been that during phase transfer of TMSHT’s, mixing potassium salt of TMSHT in water with tetraheptylammonium bromide in toluene, some KBr is also transferred into toluene. In this presentation we report new 31P NMR spectra for Co-substituted Keggin ion in toluene solution, which was washed with excess water after polyoxometalate transfer. This procedure removes majority of potassium and bromide ions, leading to simplification of NMR spectra.
Fabrication of graphitic oxide films by electrophoretic deposition

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ABSTRACT: Graphene is a two dimensional sheet of sp² hybridized carbon atoms. Graphene is a semiconductor, making it a potentially useful material for electronics. The purpose of this research was to fabricate graphitic oxide films of controlled thickness and acceptable uniformity. Graphitic oxide nanoparticles in solution were deposited on various substrates by electrophoretic deposition. The deposition was controlled by varying the current and time the current was applied. The films were then analyzed by UV-Vis, AFM, SEM and Raman spectroscopy to determine thickness, morphology and smoothness. The graphitic oxide films will eventually be reduced to graphene.
Juicing the juice: A laboratory based case study for analytical and general chemistry courses.

Frank J. Dinan, Peter M. Schaber, Renee Larson and Michael St. Phillips
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ABSTRACT: A young, inexperienced FDA chemist is asked to distinguish between authentic fresh orange juice and reconstituted orange juice falsely labeled as fresh orange juice. In a general chemistry version of this case, a fluoride ion selective electrode method is used, and in a more advanced analytical chemistry version, inductively coupled plasma (ICP) spectroscopy is used to distinguish between the fresh and reconstituted samples based on their calcium and magnesium concentrations. Students working in teams are given the challenge posed to the FDA chemist. They are charged with designing their procedure, obtaining and analyzing the needed data, and writing a report to their boss. Experimental design, student survey and assessment results are provided.
ABSTRACT: Since the initial synthesis of dialkoxy disulfides in 1895, little has been done on this functionality until very recently. This structural moiety has been shown to thermolytically decompose to liberate trappable S₂ in a pseudo Diels-Alder reaction. In addition, this functionality has also been used to attach an alkoxy radical to fullerenes. We have examined a family of benzylic dialkoxy disulfides (X-Ph-CH₂–O-S-S-O-CH₂-Ph-X) under photolytic conditions to determine a substituent effect. We have been able to show that the decomposition is autocatalyzed and follows Swain and Lupton’s field constant, $F$. In addition, the thermolytic decay was examined and the ratio of products (alcohol and aldehyde) as well as the rate of decomposition was obtained.
Hoechst binds to 1x1 nucleotide internal loops in RNA

Andrew D. Kauffmann and Jessica L. Childs-Disney

Department of Chemistry & Biochemistry, Canisius College, Buffalo, NY 14208

ABSTRACT: RNA has important biological roles such as participating in protein synthesis, regulating gene expression, and catalyzing chemical reactions. Like proteins, RNA folds into 3D structures that often provide binding pockets for small molecules, providing an opportunity for therapeutic intervention and/or modulation of function. A recent report found that Hoechst 33258 binds to 1x1 nucleotide internal loops closed by GC base pairs in RNA. Here we report the systematic mutagenesis of the loop nucleotides and the closing base pairs in order to gain insight into the molecular recognition of Hoechst and RNA loops.
A concise total synthesis of spirotryprostatin A

Peter Fuller, Daniel N. Saada, and Sherry R. Chemler
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ABSTRACT: Spirotryprostatins A and B are natural products, isolated from Aspergillus fumigatus, which possess cancer cell inhibitory properties as well as being structurally intriguing with a complex multifunctionalized core, making it a major pursuit for organic chemists. In this research project, we plan to improve upon some of the major drawbacks of the previous syntheses of Spirotryprostatin A, while displaying the organometallic chemistry developed in the Chemler lab. The copper-promoted diastereoselective cyclization reaction that was developed in the Chemler lab is integrated into one of the key steps of this reaction synthesis. The rest of the synthesis uses some interesting chemical processes and some somewhat unconventional methods of known reaction mechanism. Our retrosynthesis scheme, shown below, shows our mechanistic pathway taken in our synthesis. In the forward synthesis of this molecule, we began with a number of known chemical reactions to obtain our starting materials shown at the end of the reverse synthesis. In our first key step, the compounds undergo a Mannich type reaction, enolizing the C3 carbon of the oxindole. This next step is our grounds for displaying the copper promoted aminooxygenation reaction developed in the Chemler lab, and is also where some problems occurred. The reaction mechanism is believed to have undergone a retro-Mannich degradation and produced starting materials. This was found to be due to the incorrect diastereomer being produced during the Mannich step. Some promising efforts have been made to remedy this problem. Once this reaction is complete, the last addition of a proline is relatively well-explored chemistry, and our final, natural product will be formed.

Retrosynthesis.